Determination of Second Virial-Coefficients and Virial Equations of
Alternative Refrigerants Based on the Speed-of-Sound Measurements¹

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Tel: +81-3-5734-2180 Fax: +81-3-5734-2893 **ABSTRACT**

The equations of second virial-coefficient, B, for difluoromethane (R-32, CH₂F₂) and

pentafluoroethane (R-125, CF₃CHF₂) are derived from the speed-of-sound data measured at

temperatures from 273 K - 343 K by the present authors with an experimental uncertainty of

±0.0072 %. B-equations are possible to be used in the temperature range from 200 K to 400 K

and from 240 K to 440 K for R-32 and R-125, respectively. The B-equations with theoretically

derived second virial-coefficient values by Yokozeki, a member of our group.

A truncated virial equation of state was then developed using the determined B-equation.

The virial equation of state represents our speed-of-sound data and most of $P\rho T$ data measured

by de Vries and Tillner-Roth within ± 0.01 % and ± 0.1 %, respectively.

KEYWORDS: alternative refrigerant, equation of state, hydrofluorocarbon, R-32, R-125,

INTRODUCTION

Since the speed of sound in the dilute gases depends heavily on the ideal-gas heat capacity and the second virial-coefficients, B, the B values can be accurately determined from the speed-of-sound measurements. Hydrofluorocarbons of R-32, R125 and 1,1,1,2-tetrafluoroethane (R-134a, CH_2FCF_3) are expected to be the components of the promising binary and/or ternary mixture refrigerants to replace chlorodifluoromethane (R-22, $CHClF_2$) because of their zero ozone-depleting-potential. The speed of sound in gaseous R-32 [1, 2], R-125 [3], and R-134a [2, 4] have been measured by the present authors within an accuracy of ± 0.0072 %.

The *B* values make it possible to calculate thermodynamic properties at low temperatures and low pressures where experimental data are not available.

The B-equation of R-134a was determined recently [5,6] by a new analytical method for the determination of B-equations. In the present study, the B values are determined from the new analytical method based on the experimental speed-of-sound values for R-32 and R-125. The determined B values are compared and discussed with the reported values. A simple virial equation of state is also developed based on the determined B values. The experimental speed-of-sound and PT data are compared with the calculated values from the equations of state.

DETERMINATION OF B VALUES FROM SPEED OF SOUND

Since the detailed explanation on the data processing of the speed-of-sound measurements for the determination of the *B* values has been written in our previous papers[5,6], only a brief explanation is given in this paper. The speed-of-sound data were measured at conditions of various temperatures and pressures but the density values were not possible to be measured. On the other hand, the *B* values of the density-series virial-equation are useful to be applied for the development of thermodynamic equation of state. When we assign a prime for the virial coefficients of pressure-series virial-equation, the relation between both virial coefficients of the density- and pressure-series virial -equations are given as follows,

$$B' = \frac{B}{RT} \tag{1}$$

$$C' = \frac{C - B^2}{\left(RT\right)^2} \tag{2}$$

$$D' = \frac{D + 2B^3 - 3BC}{(RT)^3} \tag{3}$$

$$E' = \frac{E - 5B^4 + 10B^2C - 4BD - 2C^2}{(RT)^4} \tag{4}$$

By using the Eqs. (1)-(4), a pressure-series virial-equation with the virial coefficients of density-series virial-equation is derived as expressed by Eq. (5).

$$Z = 1 + \frac{B}{RT}P + \frac{C - B^2}{(RT)^2}P^2 + \frac{D + 2B^3 - 3BC}{(RT)^3}P^3 + \frac{E - 5B^4 + 10B^2C - 4BD - 2C^2}{(RT)^4}P^4$$
(5)

A Gibbs function is derived from Eq.(5) using our ideal-gas heat-capacities [2,3] and the speed of sound is derived from the Gibbs function by using a general thermodynamic relation. The virial coefficients of density-series virial-equation are possible to be directly derived by fitting the equation to the experimental speed-of-sound data with temperature and pressure values.

Before the data processing mentioned above, we examined the number of terms of virial equations for representing the $P\rho T$ properties at the same range of the present speed-of-sound data [1-3]. For almost whole gaseous phase, only two-term density-series virial-equation with the second and third virial-coefficients, B and C, is accurate enough, whereas a four-term pressure-series virial-equation with the second to fifth virial-coefficients is necessary to represent the $P\rho T$ properties at the same range of the present speed-of-sound data [1-3] with the same deviations as those of the density-series virial-equation. The necessary number of terms are the same for R-32, R-125, and R-134a.

We fitted eq.(5) with the fourth and fifth virial-coefficients of the density-series virial-equation being zero (D = 0 and E = 0) to the speed-of-sound measurements and then we could determined the second and third virial-coefficient (B and C) values. Because of the fitting range is very small region of the dilute gaseous phase, so the third virial-coefficient, C, is not possible to be accurately determined from the present speed-of-sound measurements. When we fitted eq.(5) to the speed-of-sound measurements, we used the following temperature function.

$$B = b_0 + b_1 \exp\left(\frac{b_2}{T}\right) \tag{6}$$

The determined numerical constants of Eq. (6) are summarized in Table I for both R-32 and R-125.

FORMULATION OF VIRIAL EQUATION OF STATE

A simple truncated virial equation of state, Eq.(7), is formulated by simply assigning functional forms to B and C.

$$Z = 1 + B\rho + C\rho^2 \tag{7}$$

The functional form for B is Eq. (6), and the numerical constants, b_0 , b_1 , and b_2 , are determined from the experimental speed-of-sound values. Since the contribution of C to the speed of sound at the lower pressure is very small, the C values are determined based on the available experimental $P\rho T$ values [7,8].

The functional form of C is assumed here by,

$$C = c_1 \left(\frac{c_2}{T}\right)^{\alpha} + c_3 \left(\frac{c_2}{T}\right)^{\beta} \tag{8}$$

where c_1 , c_2 , c_3 , α , and β are numerical constants. Namely, the present virial equation of state, Eq. (7), consists of four temperature and density terms as shown in Eqs. (6) and (8).

The C values could be determined so as to be consistent with the accurate experimental $P\rho T$ values by fitting Eq. (7) with Eqs. (6) and (8). For the determination of the four-term virial equations of state, the experimental $P\rho T$ values of R-32 and R-125 reported by, Zhang et al. [7], and de Vries and Tillner-Roth [8] were used. The determined numerical constants in Eq. (8) are given in Table II for R-32 and R-125 whereas the ranges of validity of Eq. (7) for R-32 and R-125 are summarized in Table III. The ranges include most of the gaseous phases for these refrigerants. The present four-term virial equation is possible to be used for the prediction of the thermodynamic properties at very low temperatures because of the reasonable behavior of the second virial-coefficients as shown in Figs. 1 and 2 as explained in the following section.

RESULTS AND DISCUSSION

Second virial-coefficients

The experimental speed-of-sound data at constant temperature are possible to be fitted by a quadratic speed-of-sound equation of the pressure-series, but the speed-of-sound data should be fitted by more complicate equation derived from eq.(5). Figures 1 and 2 show the difference between the second virial-coefficient values derived through the existing data processing and those through the present processing for R-32 and R-125, respectively.

Figure 1 shows the comparison of the second virial-coefficient, B, for R-32. The B values of

Zhang et al. [9] and de Vries and Tillner-Roth [8] for R-32 agree with Eq. (6) within ± 0.6 % and ± 1.8 %, respectively. We plotted the theoretical B values by Yokozeki et al. [10] in our group, these theoretical values agree with the present results within ± 2.0 % even at temperatures below 260 K and to those above 380 K. The previous B values [1] which have been determined through an older data processing which is also compared in Fig. 1. The previous values [1] agree with present B values within ± 2.0 % at limited temperature range, 273 K - 343 K. However, the extrapolated B values of the previous paper [1] deviate -15 % from the present values at 200 K. Because of the thermodynamic condition of R-32 is much closer to the ideal-gas condition than that of R-125, the second virial-coefficient of R-32 is not easily determined from the experimental results.

For R-125, the B values of Zhang et al. [9], Gillis [11] and Boyes and Weber [12] agree with Eq. (6) within ± 1.7 %, ± 2.4 %, and ± 0.7 % respectively, as illustrated in Fig. 2. The theoretical values by Yokozeki et al. [10] agree well with the present values within ± 0.6 % within the range of validity of the present model. Even if eq. (6) are extrapolated to the lower temperatures below 260 K as well as at higher temperatures above 390 K, the present B values agree with those by Yokozeki et al. [10] within ± 3.0 %. And we cited the previous B values [3] which have been determined by using the second acoustic-virial-coefficients in Fig. 2. The previous values [3] agree with present B values within ± 1.6 % at 240 K - 440 K because the contribution of the B values to the speed of sound is large enough to accurately determine the B values.

The virial equation of state

Figures 3 and 4 show the deviations of the experimental W data from the calculated values by the four-term virial equation of state for R-32 and R-125. For R-32, the W data [1,2] agree well with the calculated values from Eq. (5) within ± 0.006 % as shown in Fig. 3. The experimental W data [3] for R-125 agree with the calculated values from eq. (5) within ± 0.011 % as shown in Fig. 4.

The deviations of experimental PT data from the present four-term virial equation of state are shown in Figs. 5 and 6. In Fig. 5, the experimental PT data reported by Zhang et al.[7] and de Vries and Tillner-Roth [8] for R-32 agree with the calculated values from Eq. (7) within ± 0.1 % in pressure. In Fig. 6, the experimental PT data reported by de Vries and Tillner-Roth [8] for R-125 agree very well with the calculated values from Eq. (7) within ± 0.05 % in pressure. On the other hand, the data reported by Zhang et al. [7] agree with the calculated values from Eq. (7) within ± 0.20 % except four data points at higher densities along 290 K, 320 K, and 390 K isotherms.

CONCLUSIONS

We determined the second virial-coefficients from the experimental speed-of-sound data for R-32 and R-125 through our proposed data processing method. The determined second virial-coefficients agree well with the reported experimental data. Both of the present B-values for R-32 and R-125 agree with the theoretical B-values even at the temperatures far beyond the range of the speed-of-sound measurements, the temperature range from 200 K to 400 K for R-32 and the temperature range from 240 K to 440 K for R-125. The present four-term virial equation of state represents the experimental speed-of-sound and most of the PT data within ± 0.01 % and ± 0.1 % in pressure, respectively.

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Table Captions

Table I: The numerical constants of Eq. (6) for R-32, R-125

Table II: The numerical constants of Eq. (8) for R-32, R-125

Table III: The available range of the present equation of state, Eq. (7), for R-32, R-125

Figure Captions

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Fig. 1: The second virial-coefficients for R-32
, Zhang et al. [9]; , de Vries and Tillner-Roth [8];
, Yokozeki et al. [10]; , Hozumi et al. [1];
, Calculated values from Eq. (6)

Fig. 2: The second virial-coefficients for R-125

Zhang et al. [9]; Gillis [11]; Boyes and Weber [1]
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- , Zhang et al. [9]; ,Gillis [11]; Boyes and Weber [12]; , Yokozeki et al. [10]; , Hozumi et al. [3];
 - , Calculated values from Eq. (6)
- Fig. 3: The deviation of the experimental W values from the calculated values by Eq. (5) for R-32
 , Hozumi et al. [1]; , Hozumi et al. [2];, Calculated values from Eq. (5)
- Fig. 4: The deviation of the experimental W values from the calculated values by Eq. (5) for R-125
 - , Hozumi et al. [3]; , Calculated values from Eq. (5)
- Fig. 5: The deviation of the experimental $P\rho T$ values from the calculated values by Eq. (7) for R-32
 - , Zhang et al. [7]; , de Vries and Tillner-Roth [8]; , Calculated values from Eq. (7)
- Fig. 6: The deviation of the experimental $P\rho T$ values from the calculated values by Eq. (7) for R-125
 - , Zhang et al. [7]; , de Vries and Tillner-Roth [8]; , Calculated values from Eq. (7)

Table I The numerical constants of Eq. (6) for R-32, R-125

| 1 \ / | | | | |
|--|---------|----------|--|--|
| | R-32 | R-125 | | |
| b ₀ , cm ³ mol ⁻¹ | 75.183 | 194.42 | | |
| b ₁ , cm ³ mol ⁻¹ | -40.088 | -109.405 | | |
| b ₂ , K | 667.86 | 489.41 | | |

Table II The numerical constants of Eq. (8) for R-32, R-125

| 1 () | | | | |
|--|------------------------|------------------------|--|--|
| | R-32 R-125 | | | |
| c_1 , $dm^6 mol^{-2}$ | 2.357×10^{-2} | 1.107×10^{-2} | | |
| c ₂ , K | 310.94 | 489.41 | | |
| c ₃ , dm ⁶ mol ⁻² | -1.50×10^{-4} | -1.46×10^{-5} | | |
| α | 3.354 | 2.426 | | |
| β | 16.41 | 13.27 | | |

Table III The available range of eq. (7), for the present refrigerants

| | <i>T</i> , K | P, MPa | ho, kg m ⁻³ |
|-------|--------------|---------|------------------------|
| R-32 | 263-383 | 0 - 6.0 | 0 - 150 |
| R-125 | 263-390 | 0 - 4.0 | 0 - 300 |

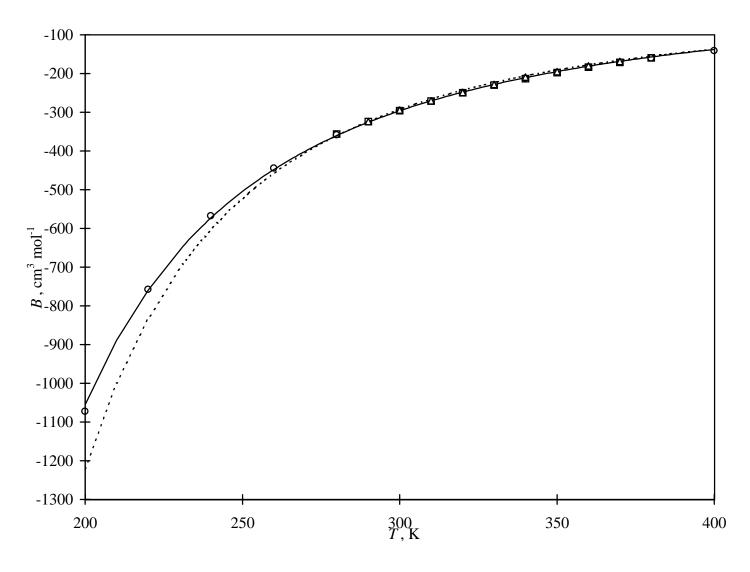


Figure 1

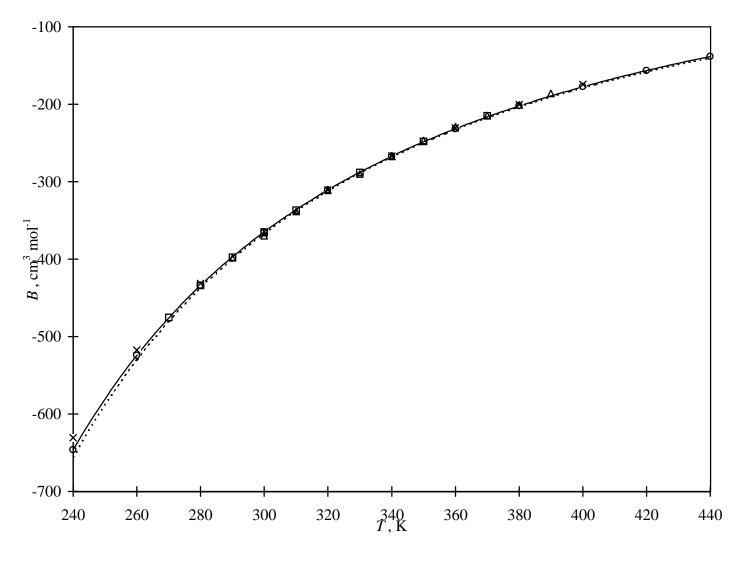


Figure 2

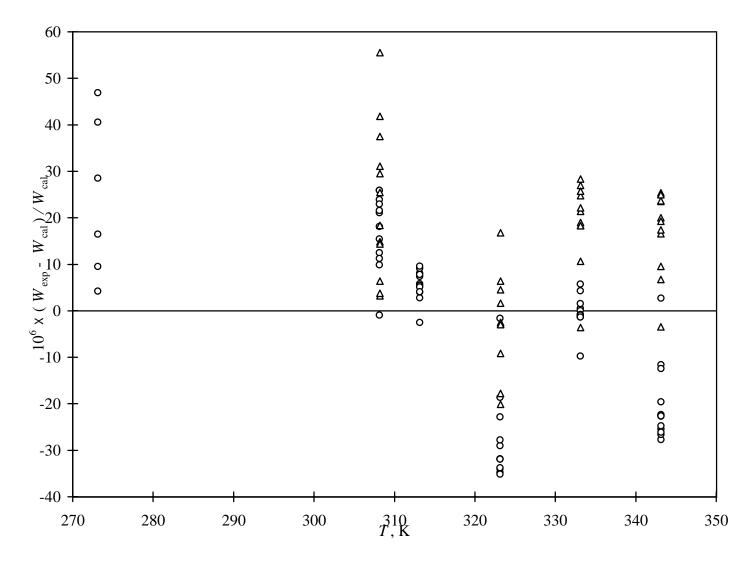


Figure 3

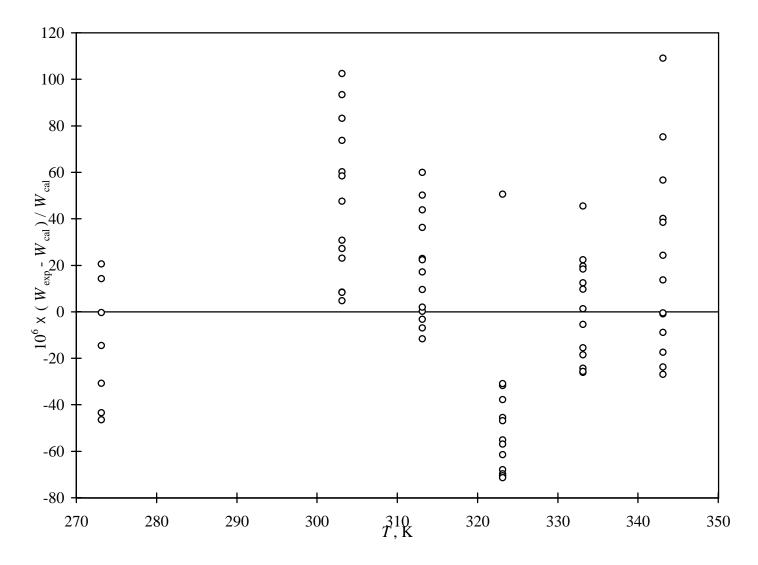


Figure 4

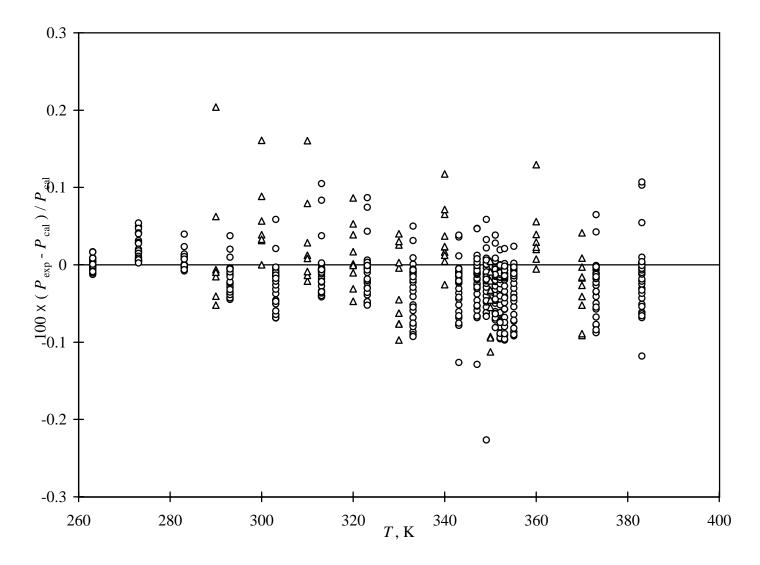


Figure 5

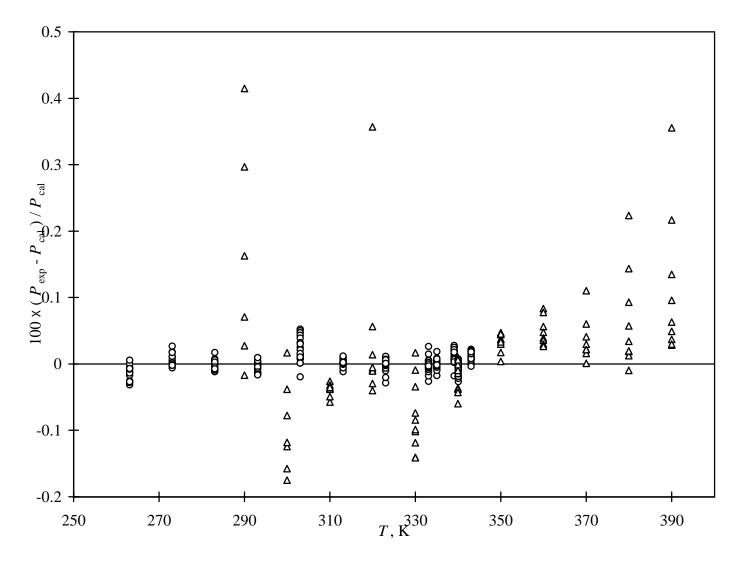


Figure 6